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COMPLETE SPECIFICATION

Water-Soluble Phenol-Aldehyde Condensation Products

We, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, a body corporate organised under the Laws of Germany, of Leverkusen-Bayerwerk, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new water-soluble condensation products and to processes for preparing the same.

The water-solubility of synthetic phenolic condensation products depends very often upon the presence of sulphonic acid groups (anionic condensation products). In many cases the accumulation of phenolic hydroxyl groups is great enough to secure sufficient water-solubility. In co-pending Application No. 19170/51 (Serial No. 747,092) there are described phenolic condensation products, the water-solubility of which is caused by the presence of salt-forming groups of basic nature. Compared with the SO_3H -containing condensation products the charge of the aforesaid phenolic condensation products is reversed (cationic condensation products).

The solubility of natural phenolic condensation products of high molecular weight is due to the accumulation of phenolic and alcoholic hydroxyl groups. Two common phenolic condensation products, viz. quebracho ordinary extracted from the wood of certain trees, and lignin forming the main part of wood cells and plant fibres, can be converted into soluble sulphonic acids by reaction with bisulphites. These high molecular weight vegetable phenolic condensation products have gained considerable technical importance as tanning agents and auxiliary tanning agents. Cationic tanning agents of vegetable origin, however, are unknown up to the present. We have now found that both anionic and cationic water-soluble phenolic condensation products can be obtained in a simple manner from one and the same water-insoluble synthetic phenolic condensation product, hereinafter called "intermediate product." The reaction

of the invention is carried out by simple heating of the intermediate products which are more fully described below, in the presence of water, with 1 mol or less of salts of sulphurous acid or polyhydric phenols or mixtures of these salts and phenols representing up to 1 mol, or salts of aromatic amines, the amount of 1 mol or less being per mol of the aldehydes used in the manufacture of the intermediate products.

The water-insoluble, high molecular weight condensation products, herein called intermediate products, are obtained by condensing resorcinol with substantially 1 mol of α,β -unsaturated aldehyde (calculated as the pure aldehyde) for every 2 mols of resorcinol, acrolein and crotonaldehyde being preferred in a concentrated aqueous solution of the reactants in the presence of mineral acids as catalysts. In practice, an exact 2:1 molar ratio of the reactants may not be convenient, a slight excess of aldehyde, for example, being used in order to allow the reaction to proceed to completion. In a more or less strongly exothermic reaction the whole reaction mixture including the water solidifies to an amorphous product which is slightly soft at 100°C and hard at room temperature. These condensation products are insoluble in water and most organic solvents, generally also in dilute alkali. The products swell, however, in dilute alkali, especially if the condensation products have been previously substantially dehydrated by drying. The condensation products gradually dissolve in an excess quantity of concentrated alkali. When the condensation is carried out in organic solvents, such as alcohols, ethers and esters, the polycondensation products are formed in a far more vigorous reaction, so that greater dilution and cooling of the reaction mixture is required.

Said insoluble, amorphous intermediate products are obtained according to the invention from resorcinol. Other polyhydricphenols appear to be less suitable for preparing the condensation products. However, the invention allows of replacing a portion of the

resorcinol by equimolecular amounts of other phenols, particularly polyhydric phenols. For instance if polyhydric phenols like pyrogallol or pyrocatechol are used, up to two-thirds of the resorcinol can be thereby replaced; if the other phenol is monohydric, up to one-third of the resorcinol may be replaced. In these reactions 1.1-bis-(dihydroxyphenyl)-propene-2 and -butene-2 respectively, which readily polymerize to insoluble intermediate products, are believed to be primarily formed.

The conversion of said water-insoluble intermediate products into water-soluble products according to the invention is mostly carried out in the boiling water-bath, more quickly under reflux. Sulphitation is performed in closed vessels, frequently at temperatures above 100°C, if necessary by applying pressure. When using 1 mol of a salt of sulphurous acid, or 1 mol of a polyhydric phenol, or 1 mol of a salt of an aromatic amine, per mol of the unsaturated aldehyde used, condensation products of the lowest possible molecular weight are formed by depolymerization. The use of less than 1 mol of the aforesaid substances, however, results in more viscous products of a higher molecular weight. Thus, the present invention offers the possibility of producing condensation products of varying molecular weight and viscosity.

The three types of water-soluble condensation products resulting from the intermediate products by reaction with the above said substances may be used as tanning agents and represent the above described types of water-soluble phenolic condensation products, viz. anionic SO₂H-containing synthetic tanning agents, tanning agents derived from polyhydric phenols, and the synthetic amino groups containing cationic tanning agents (cationic tanning agents).

Another way of preparing the new water-soluble condensation products consists in reacting aqueous solution of 1 mol of an α,β -unsaturated aldehyde and 2 mols of resorcinol —part of the resorcinol may be replaced by other phenols, preferably polyhydric phenols —with the addition of at most one mol of a bisulphite or a polyhydric phenol or a mixture of these, or a salt of an aromatic amine in the presence of a small quantity of a mineral acid in the boiling water bath. This process is carried out in one single reaction without isolation of the water-insoluble intermediate products. The viscosity, proportional to the molecular weight, and the solubility of the resulting products depend on the additional amounts of bisulphites, polyhydric phenols or salts of aromatic amines, which may be employed in quantities not exceeding 1 mol, to such an extent that the addition of 1 mol of said substances gives rise to products of lowest viscosity (molecular weight) and best solubility, whereas the above described insoluble, high molecular weight intermediate products

are obtained without the addition of any of the aforesaid substances. The invention thus allows of controlling the viscosity and solubility of the new products by varying the amounts of the additional substances within the range from greater than 0 up to 1 mol, in practice 0.125 to 1 mol.

The reaction is believed to proceed in such a manner that the condensation products form by polymerization of the probably initially formed 1.1-bis-(dihydroxyphenyl)-butene-2 or -propene-2, the chain however, is prematurely interrupted by the polyhydric phenols or salts of aromatic amines or bisulphite employed in quantities ranging from greater than 0 up to 1 mol, in practice 0.125 to 1 mol.

Quebracho ordinary, the best known natural tanning agent, can be adjusted to any desired degree of solubility by sulphitation. The present invention (regardless as to whether, during reaction, the water-insoluble condensation products, the so-called intermediate products, are isolated or not) constitutes great advantages since the process is not restricted to sulphitation and, in consequence thereof, to the production of anionic condensation products, but as already mentioned above allows of producing products, which are similar to the tannins of vegetable origin, by simple reaction with polyhydric phenols. In this reaction it is easy to vary the properties of the resulting products as regards colour and solubility, in accordance with the wishes and requirements of the tanneries, by suitable choice and control of the quantity of the polyhydric phenols. By the reaction of the salts of aromatic amines, which is likewise easily carried out, a new type of cationic tanning agent is eventually obtained. These tanning agents which are soluble in alkalies and acids —except at the neutral pH—completely precipitate the two other types of tanning agents and therefore are preferably employed as retanning agents.

According to analysis the new tanning agents contain about 4 grams of pure tannin per litre and contain a percentage of pure tannin in the dried substance of mostly above 90, often above 95, which shows that the reaction of the intermediate products to form the new water-soluble products almost proceeds quantitatively. The leather treated with the three types of tanning agents obtained according to the invention shows very good properties. The solution in which the leather is tanned and retanned with cationic tanning agents is preferably neutralized to a pH-value towards 5.

The following Examples are given for the purpose of illustrating the invention: in some of the Examples a slight excess of aldehyde is used to allow the reaction to proceed to completion.

EXAMPLE 1.

A solution of 110 grams of resorcinol and

- 100 ml. of water, which is cooled to 15°C, is mixed with 35 grams of technical acrolein (about 80% pure aldehyde); thereafter 2 ml. of hydrochloric acid (1:1) are added at 10°C with ice-cooling and stirring. The temperature quickly rises towards 70°C. The mixture is slowly heated up in the water-bath, the strong smell completely disappears, the homogeneous solution becomes more and more viscous and solidifies after some minutes. The mixture is heated thereafter for a further 15 minutes. For further reaction the high molecular weight, insoluble product is reduced to small pieces, preferably in a hot condition
- b) REACTION WITH A POLYHYDRIC PHENOL
The insoluble intermediate product is mixed with 54 grams of resorcinol (or 54 grams of catechol or 62 grams of pyrogallol) with the addition of 50 ml. of water in the boiling water-bath. The aqueous portion of the mixture is initially completely adsorbed by the insoluble portion so as to form a gel. It then quickly fuses together and liquefies. After 2 hours heating a rather thinly liquid solution is obtained which is miscible with water in all proportions. Before using the solution as tannin the small quantity of mineral acid is neutralized with ammonia.
- a) SULPHITATION
The insoluble product obtained as described above is heated with 50 grams of sodium bisulphite and 100 ml. of water in a pressure flask in the boiling water-bath. The aqueous portion of the mixture is initially completely adsorbed by the insoluble portion. It then gradually fuses together, liquefies and becomes completely homogeneous and thinly liquid after about 2 hours. The mixture has to be shaken frequently. The total duration of heating amounts to about 6—8 hours. The product thus obtained is soluble in water in all proportions. Sulphitation may also be carried through with half of the bisulphite within the same reaction time. By decreasing the amount of bisulphite but using the same quantity of water it is preferable to carry out the reaction at 120—130°C.
- c) REACTION WITH THE SALT OF AN AROMATIC AMINE.
The insoluble intermediate product is mixed while stirring with 64 grams of aniline hydrochloride and 60 ml. of water in the boiling water-bath. After adsorption of the aqueous portion of the mixture by the insoluble product the mass quickly fuses together and becomes soon thinly liquid and homogeneous. After 2 hours heating a product is obtained, which is soluble in water in all proportions. The reaction carried out for instance with 90 grams of α -naphthyl amine hydrochloride with the addition of 100 ml. of water proceeds similarly. Before using the solution as tannin the mineral acid employed in the reaction as catalyst has to be neutralized with ammonia. The products obtained by the reaction according to b) and c) show, as tanning solutions, the following analytical values:

70	Reaction with:	catechol:	aniline hydrochloride:	α -naphthyl amine-hydrochloride:	p-chloro-aniline-hydrochloride:	as-m-xylidine-hydrochloride:	carmidine hydrochloride:
	Concentration	55.7%	55.1%	52.2%	41.3%	44.0%	49.6%
	Tannins	51.9%	51.7%	50.0%	40.1%	43.3%	54.3%
75	Percentage of pure tannin in dry substance	93.3	93.8	95.9	97.0	98.0	91.4
	Acid number	3	79	61	51	54	56
	pH-value	3.96	3.24	2.9	3.53	4.0	3.9
80	weight of sample per litre	8.0g	8.0g	9.0g	10.0g	10.0g	10.0g
	=grams of pure tannin per litre	4.15g	4.14g	4.5g	4.01g	4.3g	4.5g

EXAMPLE 2.

A solution of 73 grams of resorcinol and 42 grams of pyrogallol with 100 ml. of water is mixed with 35 grams of technical acrolein (about 80% pure aldehyde) and reacted with 2 ml. of hydrochloric acid (1:1) at 10°C with ice-cooling and stirring. The temperature quickly rises between 65 and 70°C. The mixture is slowly heated up in the water-bath, the strong smell soon disappears and the reaction mixture solidifies in the boiling water after some minutes. Heating is then continued in the vivaciously boiling water-bath for 15 minutes.

15 a) SULPHITATION.

The intermediate product reduced to small pieces in a hot state is heated with 26 grams of sodium bisulphite and 100 ml. of water in a pressure flask in the boiling water-bath while frequently shaking. The reaction proceeds in exactly the same way as described in Example 1 a). After the mixture has become completely homogeneous heating is continued

for another hour. The thinly liquid solution is miscible with water in every proportion.

b) REACTION WITH POLYHYDRIC PHENOLS.

The intermediate product is heated while stirring with 55 grams of resorcinol and 60 ml. of water in the boiling water-bath. The reaction proceeds in exactly the same way as described in Example 1 b). After 2 hours a product is obtained which is soluble in water in all proportions.

c) REACTION WITH SALTS OF AROMATIC AMINES.

The intermediate product is heated with 71 grams of o-toluidine hydrochloride and 65 ml. of water in the boiling water-bath. The reaction proceeds in exactly the same way as described in Example 1 b). After 2 hours heating the solution is miscible with water in all proportions. Before using at tannin the solution is neutralized with some ammonia. The products prepared for instance according to b) and c), show, as tannin solutions, the following analytical values:

	b)	c)
Concentration	54.6%	52.9%
Tannins	51.0%	49.7%
Percentage of pure tannin in dry substance	93.3	93.8
Acid number	9.2	84.0
pH-value, analytical strength	3.5	3.0
Weight of sample	9 grams = 4.6 grams of pure tannin per litre	9 grams = 4.45 grams of pure tannin per litre

EXAMPLE 3.

A solution of 110 grams of resorcinol in 100 ml. of water and 37 grams of crotonaldehyde (b.p. 99—105°C) is reacted with 10 ml. of hydrochloric acid (1:1) or 2 ml. of concentrated sulphuric acid + 2 ml. of water at 30°C with stirring. The temperature rises towards 80°C within 10 minutes, the strong smell soon disappears and the solution becomes more and more viscous and finally solidifies. The mixture is heated thereafter in the boiling water bath at an internal temperature of 95—100°C for 15 minutes. Before carrying on reaction the resultant cake is reduced to small pieces, preferably in a hot condition.

a) SULPHITATION.

The insoluble intermediate product is heated with 25 grams of sodium bisulphite and 100 ml. of water in the pressure tube to 120°C with frequent shaking. After 6 hours the solution is thinly liquid, homogeneous and miscible with water in all proportions.

b) REACTION WITH POLYHYDRIC PHENOLS.

The above described intermediate product is heated with resorcinol, catechol or pyrogallol. Solutions which are miscible with water in all proportions are obtained in exactly the same way as described in Example 1 b). By reducing the quantities of polyhydric phenols (to a half or a third) more viscous solutions

are obtained if the reaction and heating operation are carried out for a prolonged period.

c) REACTION WITH SALTS OF AROMATIC AMINES.

- 5 The high molecular weight intermediate product is reacted as described in Example 1 c) with aniline hydrochloride or α -naphthylamine hydrochloride with the addition of water to form a water-soluble product. The
- 10 herein described process is accessible to various modifications (similar to Example 1 c) because of the possibility of using the hydrochlorides

of equivalent quantities of primary, secondary and tertiary aromatic bases which may be halogenated or methylated in the nucleus. If, instead of aniline hydrochloride, aniline sulphate is used to solubilize the aforesaid high molecular intermediate products, the soluble products obtained are only soluble in hot water near the boiling point. Before using the solutions thus obtained as tanning or retanning agents the mineral acid employed in the reaction as catalyst has to be neutralized. Some products show, as tannin solutions, the following analytical values:

Reaction with:	Bisulphite:	catechol:	Aniline hydrochloride:	α -naphthylamine hydrochloride:	Dimethyl-aniline hydrochloride:	2-chloro-4-toluidine hydrochloride:
30 Concentration	47.0%	53.4%	57.2%	51.2%	82.4%	40.0%
Tannins	41.6%	51.3%	52.6%	49.0%	73.2%	38.4%
Percentage of pure tannin in dry substance	88.4	96.4	92.0	95.8	88.8	96.0
35 pH-value, analytical strength	3.3	2.5	3.1	2.9	3.7	3.6
acid number	20	25	91	63	116	49.3
weight of sample per litre	10.0g	10.0g	9.0g	9.0g	6.0g	11.0g
40 =grams of pure tannin per litre	4.16g	5.1g	4.7g	4.4g	4.4g	4.4g

EXAMPLE 4.

- 45 A solution of 110 grams of resorcinol in 100 ml. of water and 18 grams of technical acrolein (about 80% pure aldehyde) and 18 grams of croton aldehyde is reacted with 2—3 ml. of hydrochloric acid (1:1) at 20°C. The temperature rises slightly above 50°C and is slowly raised in the water-bath whereby a slight exothermic reaction occurs. The strong
- 50 smell disappears soon and the reaction mass solidifies after a short time and becomes highly viscous. The mixture is heated thereafter in the boiling water bath for half an hour at an internal temperature of 95°C.

a) SULPHITATION.

The insoluble intermediate product is heated with 24 grams of sodium bisulphite and 100 ml. of water in the closed tube between

120—130°C for 2½ hours. Sulphitation proceeds in the usual manner. For use as tannin the solution is adjusted, by means of glacial acetic acid, to an acid number of 50 calculated on the dry substance.

b) REACTION WITH POLYHYDRIC PHENOLS.

The intermediate product is heated with 54 grams of catechol with the addition of 75 ml. of water in the boiling water bath. After 2 hours a product is obtained which is soluble in water in all proportions.

c) REACTION WITH SALTS OF AROMATIC AMINES.

The intermediate product is heated while stirring with the addition of 63 grams of o- or p-chloro aniline to 75 ml. of water and 40—44 ml. of concentrated hydrochloric acid in the boiling water bath. The mass becomes

soon homogeneous and water-soluble. The heating operation takes 2-3 hours. As tannins the solutions according to a) and b) show the following analytical values:

5		a)	b)
	Concentration	47.3%	51.6%
	Tannins	41.0%	48.4%
	Percentage of pure tannin in dry substance	88.5	94.0
10	Acid number	50	4
	pH-value, analytical strength	3.1	3.2
15	Weight of sample	10g = 4.1g of pure tannin per litre	9g = 4.35g of pure tannin per litre

EXAMPLE 5.

A solution of 73 grams of resorcinol, 160 grams of "brenzoei," 50 ml. of water and 74 grams of croton aldehyde (representing about 1 mole of pure aldehyde) is reacted with 20 ml. of hydrochloric acid (1:1) at 10°C with stirring. The temperature rises to 90°C and the reaction mixture solidifies in the boiling water-bath to a rubber-like mass. After heating for half an hour the product can be pulverized at room temperature.

a) SULPHITATION.

The intermediate product is heated with 104 grams of sodium bisulphite and 250 ml. of water in a stirring apparatus (made of Cu or more preferably Ag) to 140°C for 12 hours. The resulting product is water-soluble in all proportions.

b) REACTION WITH POLYHYDRIC PHENOLS AND BISULPHITE.

The intermediate product is heated in the stirring apparatus with 52 grams of sodium bisulphite, 54 grams of catechol and 250 ml. of water to 140°C for 12 hours. The resultant product is water-soluble in all proportions.

c) REACTION WITH SALTS OF AROMATIC AMINES.

The intermediate product is heated with 130 grams of aniline hydrochloride and 100 ml. of water in the boiling water-bath. The reaction mixture quickly becomes liquid and homogeneous and is water-soluble in all proportions after 6 hours. The solution is neutralized by addition of 5 ml. of concentrated ammonia and another small quantity of water is added. As tannins the solutions according to a), b) and c) show the following analytical values:

55		a)	b)	c)
	Concentration	60.3%	60.0%	47.2%
	Tannins	43.2%	45.9%	42.6%
	Percentage of pure tannin in dry substance	73.0	76.6	90.3
60	Acid number	25.0	30.0	72.0
	pH-value, analytical strength	3.1	3.5	3.0
	Weight of sample	9 g	9.0 g	12.0 g
65		= 3.9g of pure tannin	= 4.1g of pure tannin	= 5.1g of pure tannin

The term "brenzoel" mentioned above denotes a part of the so-called phenolic oils which are recovered from waste liquors—formed in the low temperature carbonization process of certain lignites and pit-coals—by extraction with organic solvents. From the phenolic oils the monovalent phenols are removed by distillation. The residue is the so-called "brenzoel," which contains catechol and homologous substitution products of catechol such as homocatechol, isohomocatechol, ethyl catechol etc., further to a lesser extent also resorcinol and its homologues, as well as remnants of substituted monovalent phenols.

EXAMPLE 6.

A solution of 55 grams of resorcinol, 55 grams of catechol, 100 ml. of water, 18 grams of technical acrolein and 18 grams of croton aldehyde (b.p. 99—105° C) (the total pure aldehyde being up to at most 1 mol) is reacted with 2 ml. of hydrochloric acid (1:1) at room temperature with stirring. The temperature rises towards 50°C and is gradually increased in the water bath. After some minutes the reaction mixture solidifies with a gradual increase in viscosity and is heated thereafter at an internal temperature of 95°C for 15 minutes. Before carrying on reaction the mass is reduced to small pieces, preferably in the hot state.

a) SULPHITATION.

The insoluble intermediate product is heated to 120—130°C for 6 hours with frequent shaking, in the pressure tube with 24 grams of sodium bisulphite and 100 ml. of water in the oilbath. After 3 hours the major part of the mixture is liquid and homogeneous. The product is miscible with water in all proportions.

b) REACTION WITH POLYHYDRIC PHENOLS.

With 63 grams of pyrogallol and the addition of 100 ml. of water the insoluble intermediate product very quickly liquefies in the boiling water-bath. After 2 hours heating the reaction product is soluble in water in all proportions. As tannin the solution shows the following analytical values:

Concentration	50.4%
Tannins	46.6%
Percentage of pure tannin in dry substance	92.3
Acid number	4.0
pH-value, analytical strength	3.4
weight of sample	9 g = 4.2 grams of pure tannin per litre

c) REACTION WITH SALTS OF AROMATIC AMINES.

The insoluble intermediate product is heated with 63 grams of o- or p-chloro-aniline, 100 ml. of water and 42 ml. of concentrated hydrochloric acid in the boiling water-bath. After 2 hours the reaction product is soluble in water in all proportions.

EXAMPLE 7.

The solution of 146 grams of resorcinol, 75 grams of crude cresol, 100—120 ml. of water and 74 grams of croton aldehyde is reacted with 10 ml. of hydrochloric acid (1:1) at 15°C with stirring. The temperature rises to 70—80°C. After heating in the boiling water-bath for a short time the reaction mixture solidifies. After heating for 15 minutes the mass is reduced to small pieces in the hot condition.

a) SULPHITATION.

The insoluble intermediate product is heated in the stirring apparatus to 150°C for 6 hours with the addition of 96 grams of sodium bisulphite and 150 ml. of water. The resultant solution is miscible with water in all proportions and, after addition of a little formic acid, shown the following analytic values:

Concentration	61.5%
Tannins	48.8%
Percentage of pure tannin in dry substance	79.3
Acid number	50
pH-value, analytical strength	3.7
weight of sample	8.5 g = 4.1 g of pure tannin per litre

b) REACTION WITH POLYHYDRIC PHENOLS.

The intermediate product is refluxed in the oil bath with 55 grams each of resorcinol and a catechol and 200 ml. of water. After some hours the reaction mass is soluble in water.

c) REACTION WITH SALTS OF AROMATIC AMINES.

The intermediate product is heated in the oil bath with 128 grams of aniline hydrochloride and 200 ml. of water. Liquefaction occurs soon. After boiling under reflux for 6 hours the reaction product is soluble in water in all proportions.

EXAMPLE 8.

A solution of 110 grams of resorcinol, 100 ml. of water and 37 grams of methyl acrolein (or 45 grams of ethyl acrolein) is reacted with 10 ml. of hydrochloric acid (1:1) at 20°C.

The temperature quickly rises towards 70°C. The reaction mass is heated thereafter in the boiling water-bath for 1 hour. The viscosity increases until the mass is present in a rubber-like consistency. After cooling the mass can be pulverised

The insoluble intermediate product can be rendered water-soluble according to one of the aforescribed methods by means of sodium bisulphite, catechol or aniline hydrochloride.

EXAMPLE 9.

A solution of 110 grams of resorcinol, 165 ml. of ethyl acetate and 37 grams of croton aldehyde (or 35 grams of technical acrolein) is heated with 2 ml. of hydrochloric acid (1:1) at 5°C with ice-cooling and good stirring. The temperature rises in a few seconds to 80°C or to the boiling point of the solution. After refluxing for one hour the reaction mixture is evaporated to dryness in vacuo and in the boiling water-bath.

The insoluble product can be rendered water-soluble by means of sodium bisulphite, polyhydric phenols and salts of aromatic bases with the addition of water as described in Examples 1 and 3.

EXAMPLE 10.

A solution of 110 grams of resorcinol, 110 ml. of methanol and 70 grams of cinnamaldehyde is reacted with 6 ml. of hydrochloric acid (1:1) at 20°C with ice-cooling and stirring. The temperature rises within some seconds to the boiling point of the solution. The smell of the aldehyde has then disappeared. By heating the red-brown solution in the boiling water-bath for half an hour the solution becomes markedly viscous. Thereupon the alcohol is distilled off in vacuo and the boiling water-bath until the residue has become dry.

a) SULPHITATION.

The insoluble, high molecular weight intermediate product is heated in the pressure tube with 50 grams of sodium bisulphite and 150 ml. of water at 130°C for 7 hours with frequent shaking. The resultant solution is miscible with water in all proportions.

b) REACTION WITH POLYHYDRIC PHENOLS.

By heating the intermediate product with 55 grams of resorcinol or catechol and 200 ml. of water in the boiling water-bath liquefaction and homogenization quickly takes place.

c) REACTION WITH THE SALTS OF AN AROMATIC AMINE.

By heating the intermediate product with 64 grams of aniline hydrochloride and 200 ml. of water in the boiling water-bath the mixture quickly liquefies and gradually becomes water-soluble after previous, complete swelling of the aqueous solution. After 6

hours heating the reaction product is soluble in water in all proportions.

EXAMPLE 11.

This Example describes the production of condensation products from 3 mols of resorcinol, or from 2 mols of resorcinol and 1 mol of catechol, or from 1 mol of resorcinol and 2 mols of catechol, with 1½ mols each of acrolein; or from 2 mols of resorcinol (partly exchanged for other polyhydric phenols) and 1½ mols of acrolein and 1 mol of a polyhydric phenol.

a) A solution of 165 grams of resorcinol in 150 ml. of water is reacted while cooling with 35 grams of acrolein with cooling and below 15°C with 2 ml. of hydrochloric acid (1:1). The temperature quickly rises at the beginning above 60°C and thereafter, more slowly, to about 75°C; the strong smell of aldehyde has soon disappeared. The mixture is heated thereafter in the boiling water-bath for 2 hours. The resulting condensation product is soluble in water in all proportions.

b) A solution of 110 grams of resorcinol and 55 grams of catechol in 150 ml. of water and 35 grams of acrolein is reacted with 2 ml. of hydrochloric acid (1:1) at 10°C with stirring. The temperature rises towards 60°C and the product is heated in the boiling water-bath until it is soluble in water in all proportions, i.e. after about 15 hours. The time of condensation can be shortened by boiling under reflux.

c) A solution of 55 grams of resorcinol and 110 grams of catechol in 150 ml. of water and 35 grams of acrolein is reacted with 2 ml. of hydrochloric acid (1:1) below 15°C. The temperature rises towards 70°C within some minutes. Heating is continued in the boiling water-bath. After about 25 minutes the reaction mixture solidifies, however quickly liquefies on heating in the oil-bath. The mixture is boiled under reflux until the product is water-soluble in all proportions, i.e. after about 20 hours. According to analysis the products obtained according to a), b) and c) contain more than 4 grams of pure tannin per litre and show percentage figures between 95—100.

EXAMPLE 12.

This Example describes the production of condensation products as indicated in Example 11, however, while using 1 mol of croton aldehyde instead of 1½ mols of acrolein.

a) A solution of 165 grams of resorcinol in 125 cc. of water is mixed at 25°C with 37 grams of croton aldehyde (b.p. 90—105°C) and at 30°C, 8 ml of hydrochloric acid (1:1) are added with stirring. The temperature rises to 90°C within 10 minutes. The smell of aldehyde quickly disappears.

The reaction mixture is heated thereafter in the boiling water-bath for 2—3 hours and is then water-soluble in all proportions.

b) A solution of 110 grams of resorcinol and 55 grams of catechol in 115 ml. of water and 37 grams of croton aldehyde is reacted with 10 ml. of hydrochloric acid (1:1) at 30°C. The temperature rises above 80°C within 15 minutes. By stirring in the boiling water-bath for 3 hours the product becomes water-soluble in every proportion.

c) A solution of 55 grams of resorcinol and 110 grams of catechol in 100 ml. of water and 37 grams of croton aldehyde is reacted with 10 ml. of hydrochloric acid (1:1) with stirring at 30°C. The temperature rises to 70°C within 20 minutes. After heating in the boiling water-bath for some minutes the reaction mixture solidifies but liquefies again after $\frac{1}{2}$ hour. After heating in the boiling water-bath for 6 hours the product is soluble in every proportion. In the reaction according to b) and c) the catechol or resorcinol may be replaced by the equivalent amount of pyrogallol. After neutralizing the solutions obtained according to a), b) and c) with a little ammonia the products show excellent tanning properties. According to analysis the tannin solutions have percentage figures of about 95 and contain 4 grams of pure tannin per litre.

EXAMPLE 13.

This Example describes the production of condensation products from 5 mols of resorcinol, or from 4 mols of resorcinol and 1 mol of catechol, or from 3 mols of resorcinol and 2 mols of catechol, with 2 mols of croton aldehyde; or from 2 mols of resorcinol (partly exchanged for other polyhydric phenols) and 1 mol of croton aldehyde and $\frac{1}{2}$ mol of a polyhydric phenol.

a) A solution of 138 grams of resorcinol in 100 ml. of water and 37 grams of croton aldehyde prepared in a manner analogous to that of Example 12 a) is reacted with 5 ml. of hydrochloric acid (1:1) at 30°C with stirring. The temperature rises towards 80°C within 15 minutes and the mixture is heated up in the boiling water-bath until the product has become soluble in water in all proportions, i.e. after about 5—6 hours.

b) A solution of 110 grams of resorcinol and 28 grams of catechol in 100 ml. of water and 37 grams of croton aldehyde is reacted with 5 ml. of hydrochloric acid (1:1) at 30°C. The temperature rises to about 70°C within 20 minutes. The mixture is heated thereafter in the boiling water-bath until the resultant product is soluble in water in all proportions, i.e. after at most 6 hours.

c) In a solution of 83 grams of resorcinol and 55 grams of catechol in 100 ml. of water and 31 grams of crotonaldehyde, 5 ml. of hydrochloric acid (1:1) are run at 30°C with stirring. The temperature rises slightly above 60°C within almost $\frac{1}{2}$ hour. The mixture is heated thereafter in the boiling water-bath. The condensation product is water-soluble in

all proportions. By neutralizing with a little ammonia and, if necessary, increasing the acid number by addition of a very small quantity of glacial acetic acid the solutions show excellent tanning properties. According to the usual tannin analysis the solutions have percentage figures above 90—96 and contain 4 grams of pure tannin per litre.

EXAMPLE 14.

This Example describes the production of condensation products from 2 mols of resorcinol and 1 mol of croton aldehyde or from 4 mols of resorcinol and 2 mols of croton aldehyde or from 8 mols of resorcinol and 4 mols of croton aldehyde with 1 mol each of aniline hydrochloride; or from 2 mols of resorcinol and 1 mol of croton aldehyde and 1 mol or $\frac{1}{2}$ mol or $\frac{1}{4}$ mol of aniline hydrochloride.

To prevent condensation of the salt of the aromatic amine with the unsaturated aldehyde or chemical addition of bisulphite (see Example 15) to the unsaturated aldehyde, 2 mols of resorcinol (partly replaced by other polyhydric phenols) are condensed first with 1 mol of the unsaturated aldehyde until disappearance of the strong smell without polymerization to insoluble products occurring, and the salts of aromatic amines or bisulphite are subsequently added and the reaction mixture is telomerized.

a) A solution of 110 grams of resorcinol in 100 ml. of water and 37 grams of croton aldehyde is reacted with 3 ml. of hydrochloric acid (1:1) with stirring at 30°C. The temperature rises to about 75°C within half an hour; the thinly liquid reaction mass is stirred thereafter at decreasing temperature for about 15 minutes, whereby the smell of aldehyde completely disappears. Thereupon the hot solution of 64 grams of aniline hydrochloride in 60 ml. of water is added and the mixture is heated in the boiling water-bath for about 3 hours. The product obtained is soluble in water in all proportions.

b) A warm solution of 32 grams of aniline hydrochloride in 35 ml. of water is poured at 60°C into the condensation product prepared according to a) from resorcinol and croton aldehyde. In the boiling water-bath the reaction mass becomes highly viscous and gradually thinly liquid again. After 5 hours heating the condensation product is water-soluble in all proportions.

c) The thinly liquid condensation product prepared according to a) from resorcinol and croton aldehyde is mixed at 60°C with the warm solution of 16—17 grams of aniline hydrochloride in 30 ml. of water and further heated in the boiling water-bath. The reaction product becomes soon viscous to such an extent that it can hardly be stirred any longer; the product liquefies again, however, during about $1\frac{1}{2}$ hours and becomes completely homogeneous. Thereupon 25 ml. of water are added to lower the viscosity. After 6 hours

heating in the boiling water-bath the condensation product is water-soluble in all proportions but more viscous than the products obtained according to a) and b). According to analysis the product obtained according to a) contains 4 grams of pure tannin per litre and shows a percentage figure of 96.

EXAMPLE 15.

This Example describes the production of condensation products from 8 mols of resorcinol or 6 mols of resorcinol and 2 mols of catechol with 4 mols of croton aldehyde and 1 mol of sodium bisulphite; or from 2 mols of resorcinol or $1\frac{1}{2}$ mols of resorcinol and $\frac{3}{4}$ mol of catechol and 1 mol of croton aldehyde and $\frac{1}{4}$ mol of sodium bisulphite.

a) The solution of 110 grams of resorcinol in 100 ml. of water and 37 grams of croton aldehyde is reacted with 4 ml. of hydrochloric acid (1:1) with stirring at 30°C. The temperature rises towards 80°C within 15–20 minutes. By stirring the reaction mixture for a further some minutes the smell of aldehyde disappears; thereupon a solution of 2 grams of sodium sulphite and 11 grams of sodium bisulphite in 30 ml. of water is added. The mixture is heated thereafter in the boiling water-bath until the product is water-soluble in all proportions, i.e. after about 7 hours. The solution is thinly liquid.

b) The solution of 82 grams of resorcinol and 28 grams of catechol in 100 ml. of water and 37 grams of croton aldehyde is reacted with 5 ml. of hydrochloric acid (1:1) with stirring at 30°C. The temperature rises to 60°C within almost $\frac{1}{2}$ hour and the reaction mixture is then heated to 80°C. The smell of aldehyde practically disappears after some minutes. The solution of 2 grams of sodium sulphite and 11 grams of sodium bisulphite in 30 ml. of water is added and the mixture is heated in the boiling water-bath until the

product is water-soluble in all proportions, i.e. after about 20 hours. After heating for 10 hours diluted solutions are still opalescent. The solution is thinly liquid.

According to analysis the solutions according to a) and b) contain 4 grams of pure tannin per litre and show percentage figures between 85 and 90.

What we claim is:—

1. Process for the production of water-soluble condensation products which comprises condensing, in the presence of water, resorcinol with substantially 1 mol of an α - β -unsaturated aldehyde for every 2 mols of resorcinol and, per mol of aldehyde, at most 1 mol of a salt of sulfurous acid or of a polyhydric phenol or of a mixture of such a salt and such a phenol, or of a salt of an aromatic amine.

2. Process as claimed in Claim 1 in which up to $\frac{1}{3}$ molar proportion of the resorcinol is replaced by a substantially equimolecular amount of a monohydric phenol.

3. Process as claimed in Claim 1 in which up to $\frac{2}{3}$ molar proportion of the resorcinol is replaced by another polyhydric phenol.

4. Process as claimed in Claim 1, 2 or 3 which comprises condensing resorcinol, or the mixture of resorcinol and another phenol in a suitable solvent, especially water, with an α - β -unsaturated aldehyde to produce a water-insoluble product isolating this product and then condensing it with a salt of sulfurous acid or a polyhydric phenol or a mixture thereof or a salt of an aromatic amine in the presence of water.

5. Process for the production of water-soluble condensation products substantially as described in any of the foregoing Examples.

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